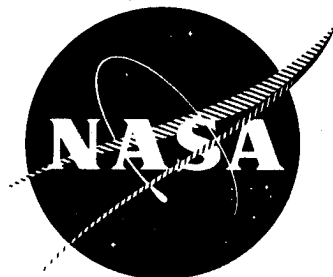


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DEVELOPMENT OF LARGE DIAMETER CARBON MONOFILAMENT

by B.A. Jacob and R.D. Veltri

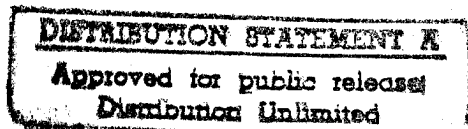
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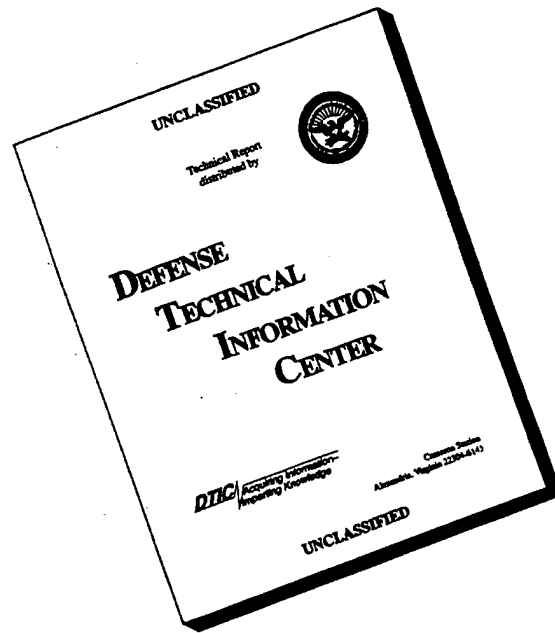


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| 16. Abstract <p>(A process for preparing large-diameter carbon-boron monofilament was developed. The process involves chemical vapor depositing a carbon-boron alloy monofilament from a BCl_3, CH_4, and H_2 gas mixture onto a carbon substrate.)</p> <p>(Amorphous alloys were formed when gaseous mixtures containing greater than 20 percent methane (80 percent BCl_3) were used. The longest uninterrupted lengths of carbon-boron monofilament were produced using a CH_4/BCl_3 gas ratio of 2.34. It was found that the properties of the carbon-boron alloy monofilament improved when the carbon substrate was precleaned in chlorine.)</p> <p>(The highest strength monofilament was attained when a CH_4/BCl_3 gas volume ratio of 0.44 was used. The average strength of one run was over 345 kN/cm^2 (500 ksi), and the modulus was over $28 \times 10^6 \text{ N/cm}^2$ ($40 \times 10^6 \text{ psi}$). While the highest strengths were attained in this run, the 0.44 gas ratio and other CH_4/BCl_3 ratios less than 2.34 would not yield long runs. Runs using these ratios were usually terminated because of a break in the monofilament within the reactor.</p> <p>It is felt that better process control could probably be achieved by varying the amount of hydrogen; the BCl_3/H_2 ratio was kept constant in these studies.</p> | | | | | |
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BCl₃ Boron trichloride
CH₄ methane
H₂ hydrogen

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SUMMARY

The purpose of this work was to develop a process for preparing large-diameter carbon monofilament. The process selected involved chemical vapor deposition using boron trichloride, methane and hydrogen gases and a conventional boron type reaction in which the substrate is resistively heated.

Amorphous carbon-boron alloys were formed when gas mixtures containing greater than 20 percent methane (80 percent BCl_3) were used. The strongest carbon-boron monofilament was achieved using a CH_4/BCl_3 gas ratio of 0.44. This gas ratio produced a monofilament in which the average composition of the deposit was 75 w/o boron and 25 w/o carbon. When this high an amount of boron is attained, it is suspected that the deposit reacts more readily with the impurities present on the surface of the carbon substrate.

The carbon-substrate fiber was precleaned in chlorine and used as a substrate. With the precleaned substrate, the strength of the carbon-boron alloy monofilament was considerably improved.

The experimentation showed that high strength, high modulus carbon-boron alloy monofilament can be produced from a BCl_3 , CH_4 , and H_2 gas system. The modulus of the monofilament appears to be linearly dependent upon the percent of boron in the monofilament.

Neither the mechanical properties of the monofilament at elevated temperature nor the mechanical properties of composites fabricated using this monofilament were determined in this investigation.

In these investigations, the BCl_3/H_2 ratio was held constant while the BCl_3/CH_4 ratio was varied. It is felt that better process control could be achieved by varying the CH_4/H_2 ratio while maintaining a constant BCl_3/CH_4 ratio.

INTRODUCTION

The object of this program was to optimize the UARL chemical vapor deposition process to produce a large-diameter, high-strength, high-modulus carbon monofilament. Parameters such as deposition temperature, substrate velocity, reactor geometry, gas ratios and total reactant gas flows were studied. The effect of variations of these parameters were noted from both property measurements such as diameter, tensile strength, Young's Modulus and density, and from the optical and electron microprobe analyses.

The program was divided into the four tasks listed:

- Task I - Process Development and Optimization
- Task II - Property Evaluation
- Task III - Reports
- Task IV - Monofilament Production and Delivery

BACKGROUND

There has been a great deal of interest recently in the development of carbon reinforcement for metal matrix applications. Most of this effort has been directed toward the use of carbon multifiber yarns and tows. Carbon yarns are becoming more readily available with various strengths and moduli and the cost of these yarns is being reduced continuously. Initially attempts were made to produce these yarns with high moduli, but recently attention has been given specifically to developing a low cost carbon yarn with little scatter in strength and modulus. As the price of these yarns has been lowered, the incentive for using carbon yarn in all types of composites has increased. Adding to the impetus to use this yarn was the fact that carbon researchers have even reported an increase in strength of carbon at elevated temperatures. The low cost of carbon yarn made it attractive for use in aluminum and its high temperature properties has induced researchers to consider it for use in high temperature matrices such as nickel.

For the past several years there has been a great deal of effort directed toward producing carbon-aluminum and carbon-nickel composites. With any metal matrix one of the most difficult problems has been to impregnate the yarn with metal matrices so that the individual fibers in the yarn would be evenly dispersed. There is also an additional problem that the fibers are easily deteriorated by reactions with the matrix material. If attempts are made to coat the fibers with barrier layers care has to be taken that the small carbon fibers are not affected by diffusion of the coating into the body of the fiber.

Although some success has been obtained in forming carbon yarn-aluminum composites (Ref. 1), these composites still do not have properties competitive with those of boron-aluminum composites containing relatively large boron filaments.

The relative advantages and disadvantages of using carbon multifiber yarns and tows versus using carbon monofilaments have been discussed in Ref. 2. Fabrication problems would be greatly reduced when large diameter carbon monofilaments are used. Composite fabrication techniques currently used with boron filaments could be transferable and the broad background of boron-aluminum composite experience could be utilized, instead of being forced to develop a whole new technology based upon small diameter carbon multifiber yarns and tows. In addition, protective coatings could be applied much more easily on large diameter monofilaments. Also, the relative fraction of coating material to filament area would be much less for the monofilaments, thus increasing the effective volume fraction of usable reinforcement and lessening the effect of the coating on the properties of the composite.

In an effort to obtain large diameter carbon monofilament for use as reinforcement for metal matrix composites, NASA-Lewis awarded several contracts to develop large diameter carbon monofilaments using different fabrication methods. The first method involved the impregnation with resin of commercially available small-diameter carbon yarns and tows. The resin impregnated bundles was then pyrolyzed to form a carbon yarn-carbon matrix composite monofilament (Refs. 3 and 4). Although reasonable strengths were obtained, difficulty was encountered in making these composite filaments because of nonuniform impregnation and cracking due to thermal expansion mismatches during pyrolysis.

The second approach consisted of using the chemical vapor deposition (CVD) method. Contracts were awarded to Hough Laboratory (Refs. 5 and 6). Initial work was done using a tungsten wire substrate, but it was found that better results were obtained using a carbon fiber substrate. Initially, pure pyrolytic graphite was deposited upon the substrate, but it was found that failure would occur by telescoping of the carbon layers over each other. This problem was eliminated by the addition of borane gas to the reactant hydrogen-hydrocarbon gases, which caused boron to be deposited to pin the carbon slip planes. This material contained approximately 30-40 percent boron.

UARL also has done research in the area of large-diameter carbon-base monofilaments. Attempts have been made using resin pyrolysis, direct conversion of large organic precursor fibers and the CVD process. Each technique had drawbacks, but the CVD process was selected for further study because it was felt to have the most potential for making the desired monofilament, even though the monofilaments produced were initially weak. It was decided to employ a combination of methane and boron trichloride as the reactant gases. The reactor used was similar to that used for boron filament development, Fig. 1, where the substrate is heated resistively and is drawn through mercury seals into a chamber where the reactant gases are introduced. Carbon fiber produced by Great Lakes Carbon Company was chosen as the substrate because of its low density and because of previous experience.

Previous to this contract, a cursory investigation was conducted to determine what amounts of boron addition would be particularly suitable for producing high quality carbon monofilament. Gases were used with compositions of 4%, 8%, 9%, 15%, 23%, 40%, 72%, 83%, 88% and 92% methane with BCl_3 ; hydrogen was also added. The strengths of the monofilament produced are presented in Fig. 2. The higher strength monofilaments appeared to be produced in two compositional regions, one produced from a gas containing 8% CH_4 , the other containing 72% CH_4 . X-ray investigations indicated that the boron carbide (B_4C) pattern was strongest in monofilament produced from gases with 8% CH_4 while the monofilament produced from gases with higher percentages of CH_4 appeared to be amorphous. The monofilament thus produced was a carbon-boron alloy. It was felt that it was in this compositional region that the kind of monofilaments desired would be attained. At this point the best monofilament had an overall composition of about 50% carbon and had a strength of nearly 206 kN/cm² (300 ksi) and a modulus of 28 kN/cm² (40×10^6 psi). Unfortunately monofilament of even this quality could not be produced consistently. As a consequence, a program was outlined to explore various compositions further while also trying to optimize the other processing parameters.

CONTRACT EXPERIMENTAL PROGRAM

In initial experiments, using the information attained in the preliminary study, the parameters were set up for investigations. These are presented in Table I. Temperatures from 1125°C to 1205°C, drawing rates of 0.338 to 0.507 cm/sec and methane to boron trichloride ratios from 0.44 to 10.1 (γ_1 to γ_5) were employed in a 58 cm reactor. The BCl_3/H_2 ratio was held at 1.0 and the total flow rates of 380 cc/min, 760 cc/min and 1520 cc/min were used. At a total gas flow of 1520 cc/min monofilament production could not be satisfactorily maintained, so this flow was not investigated further.

Data from these initial experiments are presented in Table II. As can be seen, the data are inconsistent. Diameters did not vary as would be expected by varying substrate velocity, and, at a fixed gas ratio and process temperature, the scatter in the average ultimate tensile strength is excessive. For these reasons, it was suspected that there was some factor which was masking the effect of the processing parameters on the monofilament strength. A prime suspect was the substrate fiber which varied in diameter and resistance due to impurities and other factors.

Surface Observations

Further insight into this problem was obtained by examining the surfaces of high quality carbon-boron monofilament, as well as some of the lower strength monofilaments by means of a light microscope. Figures 3 and 4 show photomicrographs of the surfaces of monofilaments. Examination of these surfaces indicated that the uniform small kernels were typical of the higher strength monofilaments and the

large kernels were commonly observed in low strength monofilaments with considerable scatter in their strength. Since it can be assumed that the outgrowths observed are caused by surface imperfections the approach taken of cleaning the substrate before carbon alloy deposition appeared to be a logical one. In addition, the uniformity of the kernels in higher strength fibers also indicates that good process controls are essential for producing high quality fiber.

Cleaning of the Substrate

Sections of carbon-boron alloy monofilament containing flaws and a randomly selected section of as-received carbon substrate fiber were chemically analyzed with an electron microprobe. The impurities found in the flaws of the carbon-boron alloy monofilament were Ca, K, Fe, S, Si, and Al. One flaw and the impurity associated with it is shown in Figure 5.

The impurities found on the surface of the as-received carbon substrate were Ca, K, Fe, S, Si, and Ni. Figure 6 shows a section of this fiber and the impurities associated with it.

Many attempts were made to clean the carbon substrate fiber. It was separately passed through ultrasonically agitated solutions of acids, commercial bleach, acetone, carbon tetrachloride, alcohol, and water. Two hot filament experiments were also conducted. They were: 1) passing the fiber through a reactor at a temperature of 1400°C under H₂ and, 2) passing the fiber through a reactor at a temperature of 1450°C under BCl₃. None of these methods adequately cleaned the surface of the fiber. Monofilament made from the "precleaned" substrate fiber was comparable in strength and surface appearance to monofilament made previously.

Next, the carbon fiber substrate was given the following treatments. The chlorine cleaning was done in an RF reactor.

Sample

- 1 Cleaned in chlorine at 1550°C
- 2 Cleaned in argon at 1800°C
- 3 Cleaned in chlorine at 1650°C with a further cleaning
 in hydrogen at 1560°C
- 4 Cleaned in chlorine at 1650°C and coated with carbon
 at 1580°C
- 5 Cleaned in chlorine at 1650°C and coated with carbon
 at 1600°C
- 6 Cleaned in chlorine at 1650°C

The results of the spectral scan analysis are given in Table III. These data show that all of the samples contain sulfur even after treatment of the substrate. The sulfur appears to be an integral part of the carbon substrate fiber which may or may not affect the carbon-boron alloy monofilament properties. The other impurities also could not be removed by heating the substrate in chlorine at 1550°C or by heating it in argon at 1800°C as can be seen from the results from samples 1 and 2. However, by raising the chlorine treatment temperature to 1650°C the impurities, except for sulfur, were cleaned from the monofilament. In sample 3, a hydrogen post treatment also was given to the fiber, but it is not clear that it is necessary. Samples 4 and 5 were coated with carbon in an attempt to prevent sulfur from interacting with the carbon-boron alloy during deposition, although it should be noted that sulfur has not been detected at any flaw or fracture site in the carbon-boron alloy monofilament. Fracture studies of carbon-boron alloy monofilament produced from a carbon coated substrate showed that the coating carbon appeared to introduce fracture sites either at the carbon-boron alloy-coating carbon interface or at the coating carbon-carbon substrate fiber interface. All tensile fractures of monofilament produced from carbon coated substrate fiber exhibited substrate fiber pullout and since the average tensile strengths of all runs of monofilament produced with a carbon coated substrate fiber centered around 104 kN/cm² (150 ksi), the coating was no longer used. Sample 6 cleaned only in chlorine at 1650°C and data in Table III and Figures 7 and 8 indicate that this was adequate to remove all the impurities except sulfur for this shipment of carbon substrate fiber. The flaw shown on the as-received substrate fiber in Fig. 7, is similar to the flaw shown in Fig. 6 and is an example of the worst flaw found on the fiber. The frequency of occurrence of this type of flaw varies from shipment to shipment. When a substrate having 8 to 9 of these flaws per meter (approximately 3 per foot) is cleaned in chlorine and examined, the flaws are no longer apparent. It is reasonable to assume that the impurity or impurities associated with this type of flaw reacted with Cl₂ to form a chloride and subsequently evaporated .

The photograph of the carbon substrate fiber cleaned in Cl₂ at 1650°C (Fig. 7) shows some pitting. Chlorine cleaning experiments conducted after the cleaning of the fiber shown in Fig. 7 and discussed below have shown that each lot number of carbon substrate fiber and even separate spools from the same lot may require different cleaning parameters. In retrospect, it is felt that the Cl₂ cleaned fiber shown in Fig. 7 was overcleaned and slightly etched.

The substrate fiber cleaned in chlorine at 1650°C was used to make carbon-boron alloy monofilament and the data are presented in Table IV.

The results of this study were quite promising, in that the strengths of the fibers produced on a clean substrate were quite similar. Although they were not as high as the best fiber produced, they did give some indication that consistency can be obtained with better process controls.

Comparison of Monofilament Produced from Different Substrates and Monofilament Composition Studies

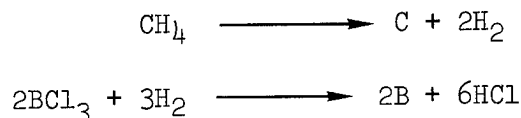
Monofilament was then made using a new spool of as-received carbon substrate fiber labeled by Great Lakes Carbon Company as Lot #1115. This spool was part of a shipment received the latter part of August. Various parameters were run and the parameters which yielded strong fibers were repeated. The data for these experiments are given in Table V.

These monofilaments obtained using a gas ratio γ_1 , were the highest strength ones produced to this point and indicated the potential of this BCl_3/CH_2 process for forming high quality fiber. The best run produced monofilament with an average strength of over 344 kN/cm^2 (500 ksi) and the individual strengths of over 462 kN/cm^2 (670 ksi). It was easily handleable, could be bent in a small radius and compared favorably with the best boron on tungsten fiber formed experimentally or in production. Unfortunately, these studies also showed that the parameters had not been well enough controlled to permit this type of high quality carbon alloy fiber to be formed reproducibly.

Since the highest strength monofilaments were obtained with CH_4/BCl_3 gas ratio of 0.44 (γ_1) with an uncleaned substrate, the next logical step was to clean the new carbon substrate which yielded the high strength monofilament and repeat the experiments. The cleaning process of 1650°C in chlorine was used because it had sufficiently cleaned the previous substrates. Unfortunately, as can be seen from the data in Table VI, monofilament with very poor properties were obtained. The appearance of the monofilament indicated that the substrate had not been thoroughly cleaned. It was at this point that it was realized that the time and temperature of the cleaning process might be quite critical, differing for various substrates, and should be investigated in detail. Because of time limitations, the cleaning temperature for the substrate was simply raised to 1720°C and fortunately considerable improvement in the properties of the carbon alloy monofilament was attained. See Table VII. The fact that the strength of the fiber was not as high as had been obtained previously was not too surprising as runs with this gas composition were difficult to control.

When gas ratio γ_1 was used, only short runs of carbon-boron alloy monofilament were attained. The runs were usually terminated by monofilament breaks within the reactor during disposition. These breaks were observed with a light microscope and breaks from two separate runs are shown in Fig. 9. The breaks are apparently caused by melted regions on the monofilaments. Assuming that these melts are low melting temperature B-X eutectics, it would follow that the greater the percent of boron in the deposit, the greater the chance of forming a eutectic. In many experiments, carbon-boron monofilament could not be produced using gas ratio γ_1 because breaks occurred shortly after the substrate fiber had been heated to the deposition temperature. Yet, when the gas ratio was changed to γ_2 , using the same substrate fiber, long runs of average quality monofilament could be produced.

Also, it was felt that the amount of hydrogen used in the gas mixture was a major factor in determining the percent of boron present in the deposit. From the reactions given below



it would be expected that increasing the hydrogen gas in the mixture would decrease the carbon content of the fiber and increase the boron content, while decreasing the hydrogen would have the opposite effect.

With these considerations in mind, a gas ratio was conceived that would yield a carbon-boron alloy monofilament in which the percent of boron in the deposit would be between that obtained from gas ratio γ_1 and γ_2 . The gas ratios for this new composition were $\text{CH}_4/\text{BCl}_3 = 1.77$, $\text{CH}_4:\text{H}_2 = 1.8$ and $\text{BCl}_3/\text{H}_2 = 1$, and was designated by the CH_4/BCl_3 gas ratio of 1.77.

To investigate the effect of H_2 on the composition of the monofilament another gas composition with the same CH_4/BCl_3 ratio, 1.77, but containing less hydrogen was established. This composition was designated 1.77' and the gas ratios were $\text{CH}_4/\text{BCl}_3 = 1.77$, $\text{CH}_4/\text{H}_2 = 4.2$ and $\text{BCl}_3/\text{H}_2 = 2.4$.

Carbon-boron alloy monofilament was produced using these new gas ratios and γ_2 . The substrate fiber used was Lot #1115 cleaned in Cl_2 at 1720°C . The data for the monofilament produced using gas ratios 1.77 and γ_2 are shown in Table VIII and the data comparing monofilament produced using gas ratios 1.77 and 1.77' are shown in Table IX.

Concurrent with the above experimentation, further experiments were conducted with gas ratio γ_2 . This ratio was chosen to produce fiber to satisfy Task IV of the contract - shipment of monofilament to NASA, and the experiments were made to optimize the strength of the monofilament while satisfying diameter requirements. Data from the experiments are shown in Table X.

The final experimentation under the contract was a series of runs to investigate the composition of the carbon-boron alloy monofilament and the modulus for that composition. Monofilament, produced from CH_4/BCl_3 ratios of 0.44 (γ_1), 1.77, and 2.34 (γ_2) were chosen for study. The properties and compositions are given in Table XI. The average weight percent boron in the deposit varied from 67 for γ_2 to 75 for γ_1 while the modulus varied from $26 \times 10^6 \text{ kN/cm}^2$ ($37 \times 10^6 \text{ psi}$) to $33 \times 10^6 \text{ kN/cm}^2$ ($49 \times 10^6 \text{ psi}$). Unfortunately, time did not permit these studies to be done with a chlorine cleaned substrate fiber.

A plot of the modulus of carbon-boron alloy monofilament as a function of w/o boron of the monofilament is given in Fig. 10. The end points of the abscissa are the average modulus of the carbon substrate fiber at 0 w/o boron and boron fiber at 100 w/o boron.

The density of monofilament from run numbers N232, 59 w/o B, N262, 65 w/o B and N266, 75 w/o B was measured by Dynatech R/D Company of Cambridge, Massachusetts. These data are shown in Table XII.

DISCUSSION

The data in Table IX shows the influence of H_2 in the H_2 , BCl_3 , CH_4 system. These data and the data in Table XI indicate the control of the monofilament composition available by varying the gas mixture. Data in Table XI show that the monofilament composition was not sensitive to deposition temperature over the range studied. Note the data from run N261 deposited at temperature T_1 and run N263 deposited at temperature T_3 .

Gas ratio 1.77 did not produce monofilament that was radically different in w/o boron from ratio γ_2 . The data in Table VIII (results of a series of experiments investigating monofilament strength as a function of temperature for gas composition 1.77 and γ_2) show a trend toward higher strength as the deposition temperature is increased. Run N238, produced using a gas ratio of 1.77 and deposition temperature of T_4 (1205°C) is exceptionally strong. Chemical analysis of this monofilament was not completed within the contract period and the reason for the anomalous diameter is not known. Cross sections of high strength monofilament showed that a fairly uniform coating of boron-carbon alloy was deposited. X-ray diffraction studies indicated that they consisted of amorphous type material.

Cross sections of monofilament produced using higher CH_4/BCl_3 gas ratios were somewhat different in that they tended to form zones of different composition during the deposition process. In early experimentation, monofilament was produced using a gas ratio γ_3 or 83% methane. The ratio of CH_4 to H_2 in gas composition γ_3 is 5 to 1 as compared with 2.34 to 1 for gas composition γ_2 . As discussed, the higher CH_4 to H_2 ratios enhances the deposition of carbon. In these experiments, the reactor clouded over and monofilament temperature could not be accurately measured. Figure 11 shows a monofilament produced from gas composition γ_3 with 246 watts applied. Note that the monofilament is starting to form zones which become more pronounced as the power to the monofilament is increased. See Fig. 12 with 264 watts applied and Fig. 13 with 300 watts applied to the monofilament. Similar results were obtained for monofilaments produced using other gas compositions with $CH_4:H_2$ ratios greater than 2.34. In each case the amount of C in the fiber increases and the tendency to form zones also increased. The reason for the multiple zones cannot be explained at this time.

The data in Table VIII and X were used to select conditions for producing monofilament to ship to NASA. The parameters were gas ratio Y_2 , Draw Speed 0.253 cm/sec (30 ft/hr) and a deposition temperature of 1185°C. Continuous lengths of 73 meters (240 ft) and 89 meters (292 ft) with average tensile strengths of 254 kN/cm² (369 ksi) and 261 kN/cm² (379 ksi) were shipped.

CONCLUSIONS

High modulus carbon-boron alloy monofilament can be chemically vapor deposited onto a carbon substrate fiber from a H_2 , BCl_3 and CH_4 gas system. Modulus is linearly dependent on the w/o boron in the monofilament. Monofilaments with composition 59 w/o boron through 75 w/o boron were amorphous. The w/o boron on the monofilament was controlled by the gas mixture and was relatively insensitive to deposition temperature over the range studied.

Studies have shown that high strength monofilament can be produced. However, as yet the parameters for forming this monofilament have not been defined. It is known that the condition of the substrate fiber is important in determining the strength of the monofilament, but the gas ratios, temperature and drawing rate must be studied further to optimize the monofilament producing process.

SUGGESTIONS FOR FUTURE WORK

The object of any future work should be to optimize the strength of a monofilament using a fixed gas ratio. Optimization of the strength would be accomplished by continued experiments on cleaning the substrate fiber, experiments to determine the best total gas flow and deposition temperature and experiments with reactor geometry (from experience with boron fiber technology, it is known that improvements in deposition can be achieved by control of gas flows and composition at various points along the fiber in the reactor). In addition, it would be meaningful to compare monofilaments produced in a direct current reactor (substrate is resistively heated through mercury contacts) with that produced in a radio frequency reactor (substrate is heated by electro-magnetic coupling to a radio frequency source) to determine which method yields the best results.

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Table I

Parameter Designation

Temperature

| Symbol | T_1 | T_2 | T_3 | T_4 |
|----------|-------|-------|-------|-------|
| Value °C | 1125 | 1150 | 1175 | 1205 |

Substrate Velocity

| Symbol | β_1 | β_2 | β_3 |
|-------------------------|------------|------------|------------|
| Value cm/sec (ft/hr) | 0.338 (40) | 0.423 (50) | 0.507 (60) |

 CH_4/BCl_3 Ratio

| Symbol | γ_1 | γ_{1a} | γ_2 | γ_3 | γ_4 | γ_5 |
|--------|------------|---------------|------------|------------|------------|------------|
| Value | 0.44 | 0.89 | 2.34 | 4.98 | 8.07 | 10.14 |

Total Gas Flow

| Symbol | X_1 | X_2 | X_3 |
|--------------|-------|-------|-------|
| Value cc/min | 380 | 760 | 1520 |

Table II - Results of Initial Deposition Experiments

| Gas Flow X ₁ | | | | Gas Flow X ₂ | | | | |
|-------------------------|----------------|------------------|-----------------------------------|-------------------------|----------------|------------------|------------------------------------|-----|
| Parameters | Run No. | Diameter μ(mils) | Avg uts KN/cm ² ksi | Parameters | Run No. | Diameter μ(mils) | Avg. uts KN/cm ² ksi | |
| γ ₂ | T ₃ | 76.2 | 137 | γ ₂ | T ₃ | 88.9 | 124 | |
| | β ₁ | 73.7 | 152 | | β ₁ | N 3 | 83.8 | 143 |
| | β ₂ | 71.1 | 131 | | β ₂ | N 6 | 78.7 | 208 |
| | β ₃ | | | | β ₃ | | 181 | |
| γ ₃ | | | | γ ₃ | | | | |
| | T ₃ | 76.2 | 111 | | β ₁ | N 12 | 88.9 | 114 |
| | β ₁ | 78.7 | 76 | | β ₂ | N 15 | 88.9 | 86 |
| | β ₂ | 63.5 | 120 | | β ₃ | 86.4 | 41 | |
| γ ₄ | | | | γ ₄ | | | | |
| | T ₃ | 66.0 | 65 | | β ₁ | N 40 | 73.7 | 101 |
| | β ₁ | 68.6 | 47 | | β ₂ | N 43 | 83.8 | 48 |
| | β ₂ | 76.2 | 43 | | β ₃ | 86.4 | 44 | |
| γ ₅ | | | | γ ₅ | | | | |
| | T ₃ | 76.2 | 37 | | β ₁ | N 49 | 88.9 | 65 |
| | β ₁ | 71.1 | 39 | | β ₂ | N 52 | 71.1 | 57 |
| | β ₂ | 66.0 | 59 | | β ₃ | 71.1 | 23 | |

Table III

Electron Microprobe Spectral Scan
Analyses of Cleaned Substrate Fiber

| Sample | Cleaning Procedure | Major | Elements Detected Minor | Trace |
|--------|--|---------------|----------------------------|------------|
| 1 | Cl ₂ 1550°C | S, Fe, Cr, Cl | Ni | --- |
| 2 | Ar 1800°C | S | --- | Fe, Si, Mn |
| 3 | Cl ₂ 1650°C and H ₂ 1650°C | S | Cl | --- |
| 4 | Cl ₂ 1650°C Carbon Deposit at 1580°C | S | --- | --- |
| 5 | Cl ₂ 1650°C Carbon Deposit at 1600°C | S | --- | --- |
| 6 | Cl ₂ 1650°C | S | --- | --- |

Table IV

Individual Tensile Tests
 (Substrate Precleaned in Cl_2 at 1650°C)
 Gage Length = 2.54 cm (1 in.)

| Run No. Parameter | N-152 $\gamma_2 \beta_{1T_3}$ | N-153 $\gamma_{1a} \beta_{1T_1}$ | N-157 $\gamma_{1a} \beta_{1T_1}$ |
|---|--|--|--|
| Diameter (μ) (mils) | 63.5 (2.5) | 59.7 (2.35) | 61.0 (2.4) |
| UTS (10^3) (N/cm^2) (psi) | 106 (153) 135 (196) 141 (204) 176 (255) 176 (255) 190 (275) 218 (316) 218 (316) 239 (346) 246 (356) | 143 (207) 151 (219) 151 (219) 151 (219) 175 (253) 175 (253) 183 (265) 210 (305) 215 (311) 223 (323) | 107 (155) 137 (199) 145 (210) 160 (232) 191 (277) 199 (288) 206 (299) 214 (310) 229 (332) 244 (354) |
| Avg. UTS (10^3) (N/cm^2) (psi) | 184 (267) | 177 (257) | 183 (265) |
| Std. Dev. UTS (10^3) (N/cm^2) (psi) | 47 (68) | 30 (43) | 44 (64) |
| Coeff. of Var. (%) | 25 | 17 | 24 |

Table V-A

Individual Tensile Tests (SI Units)
 (As-received Substrate Lot No. 1115)
 Gage Length = 2.54 cm (1 in.)

| Parameters | $\gamma_2 \beta_{1T1}$ | | $\gamma_2 \beta_{1T2}$ | | $\gamma_2 \beta_{1T3}$ | | | $\gamma_1 \beta_{1T1}$ | | | | | $\gamma_1 \beta_{1T2}$ | | |
|---|------------------------|-------|------------------------|-------|------------------------|-------|-------|------------------------|-------|-------|-------|-------|------------------------|--|--|
| Run Nos. | N-163 | N-168 | N-169 | N-170 | N-164 | N-167 | N-171 | N-173 | N-174 | N-190 | N-166 | N-176 | N-191 | | |
| Diameter (μ) | 53.3 | 63.5 | 63.5 | 68.6 | 63.5 | 66.0 | 66.0 | 63.5 | 66.0 | 63.5 | 71.1 | 78.7 | 71.1 | | |
| UTS(N/cm ² x 10 ³) | 60 | 92 | 63 | 108 | 28 | 273 | 143 | 70 | 59 | 81 | 163 | 96 | 95 | | |
| | 74 | 92 | 77 | 121 | 56 | 313 | 178 | 99 | 85 | 108 | 179 | 142 | 99 | | |
| | 74 | 99 | 110 | 121 | 91 | 314 | 182 | 106 | 91 | 119 | 202 | 146 | 109 | | |
| | 83 | 106 | 123 | 127 | 91 | 345 | 208 | 119 | 104 | 126 | 264 | 210 | 129 | | |
| | 92 | 131 | 141 | 139 | 99 | 358 | 224 | 137 | 144 | 133 | 308 | 210 | 135 | | |
| | 132 | 145 | 162 | 159 | 126 | 362 | 228 | 141 | 163 | 133 | 355 | 215 | 137 | | |
| | 159 | 162 | 197 | 213 | 130 | 371 | 243 | 183 | 163 | 133 | 371 | 219 | 140 | | |
| | 164 | 178 | 201 | 217 | 148 | 383 | 246 | 186 | 189 | 141 | 373 | 233 | 146 | | |
| | 179 | 197 | 211 | 224 | 161 | 391 | 266 | 197 | 189 | 155 | 409 | 275 | 166 | | |
| | 219 | 204 | 235 | 235 | 186 | 464 | 286 | 232 | 215 | 173 | 415 | 403 | 197 | | |
| Avg. UTS | 124 | 141 | 152 | 166 | 112 | 357 | 220 | 147 | 140 | 130 | 304 | 215 | 135 | | |
| Std. Dev. | 55 | 43 | 59 | 50 | 48 | 52 | 43 | 51 | 52 | 25 | 96 | 84 | 30 | | |
| Coeff. of Var. (%) | 44 | 31 | 39 | 30 | 43 | 15 | 20 | 35 | 38 | 19 | 32 | 39 | 23 | | |

Table V-B

Individual Tensile Tests (English Units)
 (As-received Substrate Lot No. 1115)
 Gage Length = 2.54 cm (1 in.)

| Parameters | $\gamma_2 \beta_{1T1}$ | | $\gamma_2 \beta_{1T3}$ | | $\gamma_1 \beta_{1T1}$ | | | | | $\gamma_1 \beta_{1T2}$ | | | |
|-----------------------|------------------------|-------|------------------------|-------|------------------------|-------|-------|-------|-------|------------------------|-------|-------|-------|
| Run Nos. | N-163 | N-168 | N-164 | N-170 | N-165 | N-167 | N-171 | N-173 | N-174 | N-190 | N-166 | N-172 | N-191 |
| Diameter (mil) | 2.1 | 2.5 | 2.5 | 2.7 | 1.8 | 2.6 | 2.6 | 2.5 | 2.6 | 2.5 | 2.8 | 3.1 | 2.8 |
| UTS (ksi) | 87 | 133 | 41 | 157 | 138 | 396 | 207 | 102 | 85 | 118 | 236 | 139 | 138 |
| | 107 | 133 | 81 | 175 | 197 | 453 | 258 | 143 | 123 | 157 | 260 | 206 | 143 |
| | 107 | 143 | 132 | 175 | 217 | 455 | 264 | 153 | 132 | 173 | 293 | 212 | 158 |
| | 121 | 153 | 132 | 184 | 276 | 500 | 301 | 173 | 151 | 183 | 382 | 305 | 187 |
| | 133 | 190 | 143 | 201 | 354 | 519 | 325 | 199 | 208 | 193 | 447 | 305 | 195 |
| | 191 | 210 | 183 | 231 | 374 | 525 | 330 | 204 | 236 | 193 | 515 | 312 | 198 |
| | 231 | 235 | 188 | 309 | 393 | 538 | 352 | 265 | 236 | 193 | 537 | 318 | 203 |
| | 237 | 259 | 214 | 315 | 472 | 555 | 357 | 270 | 274 | 204 | 540 | 338 | 211 |
| | 260 | 286 | 234 | 325 | 591 | 566 | 386 | 286 | 274 | 224 | 593 | 398 | 241 |
| | 318 | 296 | 269 | 341 | 591 | 672 | 414 | 336 | 311 | 251 | 602 | 584 | 285 |
| Avg. UTS | 179 | 204 | 162 | 241 | 360 | 518 | 320 | 213 | 202 | 189 | 440 | 312 | 196 |
| Std. Dev. | 79 | 63 | 69 | 73 | 158 | 75 | 63 | 74 | 76 | 36 | 139 | 122 | 44 |
| Coeff. of Var. (%) | 44 | 31 | 43 | 30 | 44 | 15 | 20 | 35 | 38 | 19 | 32 | 39 | 23 |

Table VI

Individual Tensile Tests
Substrate Cleaned under Cl_2 at $1650^\circ C$
Gage Length = 2.54 cm. (1 in)

| Run No. | N 209 | N 210 | N 211 | N 212 |
|--|--|--|--|---|
| Parameters | $\gamma_1 \beta_1 T_1$ | γ_1 0.254 cm/sec T_1 | γ_1 0.254 cm/sec T_2 | $\gamma_1 \beta_2 T_2$ |
| Diameters (μ) (mils) | 66 2.6 | 66 2.6 | 71.1 2.8 | 66 2.6 |
| UTS (10^3) (N/cm ²) (psi) | 72 104 84 123 111 160 111 160 117 170 117 170 124 179 130 189 150 217 176 255 | 111 160 130 189 136 198 150 217 150 217 169 245 176 255 182 264 189 274 221 321 | 112 162 112 162 123 179 123 179 129 187 134 195 140 203 151 219 173 252 185 268 | 91 132 117 170 117 170 124 179 130 189 130 189 137 198 137 198 137 198 150 217 |
| Avg. UTS (10^3) (N/cm ²) (psi) | 119 173 | 161 234 | 138 200 | 127 184 |
| Std. Dev. UTS (10^3) (N/cm ²) (psi) | 36 43 | 39 47 | 30 36 | 19 23 |
| Coeff. of Var. (%) | 25 | 20 | 18 | 13 |

Table VII

Individual Tensile Tests
Substrate Cleaned under Cl₂ at 1720°C
Gage Length = 2.54 cm (1 in.)

| Run Nos. | N213 | N214 | N215 |
|--|---|--|---|
| Parameters | γ β T_1 | γ β T_2 | γ β T_1 |
| Diameter (μ) (mils) | 63.5 2.5 | 66 2.6 | 68.6 2.7 |
| UTS (10^3) (N/cm ²) (psi) | 70 102 189 275 225 326 225 336 225 336 225 336 239 346 239 346 253 366 253 366 | 65 94 104 151 130 188 143 207 167 245 208 301 221 320 221 320 247 358 272 395 | 96 140 181 262 181 262 217 315 217 315 229 332 229 332 241 350 253 367 253 367 |
| Avg. UTS (10^3) (N/cm ²) (psi) | 216 314 | 178 258 | 210 304 |
| Std. Dev. UTS (10^3) (N/cm ²) (psi) | 65 78 | 80 97 | 57 69 |
| Coeff. of Var. (%) | 25 | 36 | 23 |

Table VIII

Individual Tensile Tests
 Substrate cleaned under Cl_2 at $1720^\circ C$
 Gage length = 2.54 cm. (1 in)

| Run Nos. Parameters | N 220 $\frac{1}{2}\beta_{11}^T$ | N 221 $\frac{1}{2}\beta_{12}^T$ | N 222 $\frac{1}{2}\beta_{13}^T$ | N 223 $\frac{1}{2}\beta_{11}^T$ | N 224 $\frac{1}{2}\beta_{12}^T$ | N 225 $\frac{1}{2}\beta_{13}^T$ | N 238 $\frac{1}{2}\beta_{14}^T$ |
|--|---|--|--|---|---|---|--|
| Diameter (μ) (mils) | 48.3 1.9 | 61 2.4 | 63.5 2.5 | 55.9 2.2 | 63.5 2.5 | 73.7 2.9 | 53.3 2.1 |
| UTS (10^3) (N/cm^2) (psi) | 73 105 109 159 134 194 146 212 158 229 170 247 170 247 182 265 207 300 219 317 | 114 166 114 166 145 210 145 210 152 221 152 221 168 243 168 243 175 254 198 289 | 169 245 183 265 183 265 197 286 211 306 211 306 225 326 232 337 232 337 232 337 | 18 26 73 105 105 153 123 179 127 184 140 202 154 224 163 237 172 250 172 250 | 77 112 112 163 141 204 176 255 218 316 218 316 218 316 225 327 232 336 239 347 | 99 145 115 167 167 242 219 318 219 318 219 318 224 326 230 333 230 333 245 356 | 101 147 243 353 293 426 304 441 334 485 345 500 345 500 355 515 355 515 375 544 |
| Avg. UTS (10^3) (N/cm^2) (psi) | 157 227 | 153 222 | 207 301 | 125 181 | 186 269 | 197 286 | 305 443 |
| Std. Dev. UTS (10^3) (N/cm^2) (psi) | 53 64 | 31 38 | 28 34 | 59 71 | 68 82 | 62 75 | 98 118 |
| Coeff. of Var. (%) | 28 | 17 | 11 | 39 | 31 | 26 | 27 |

Table IX

Strength and w/o Boron for Monofilament Produced
 from Gas Ratios 1.77 and 1.77'
 Substrate - GLRC Lot No. 1115 Cleaned in Cl_2 at 1720°C
 Gage Length for UTS Data is 2.54 cm (1² in.)

| Run Nos. | N 232 | | N 224 | |
|----------------------------|-----------------|-------|----------------|-------|
| Parameters | 1.77' β_1 | T_2 | 1.77 β_1 | T_2 |
| Diameter (μ)(mils) | 55.9 | 2.2 | 63.5 | 2.5 |
| UTS (10^3) | 91 | 132 | 77 | 112 |
| (N/cm ²) (psi) | 109 | 158 | 112 | 163 |
| | 127 | 184 | 141 | 204 |
| | 145 | 211 | 176 | 255 |
| | 163 | 237 | 218 | 316 |
| | 172 | 250 | 218 | 316 |
| | 172 | 250 | 218 | 316 |
| | 178 | 258 | 225 | 327 |
| | 181 | 263 | 232 | 336 |
| | 199 | 289 | 239 | 347 |
| Avg. UTS (10^3) | | | | |
| (N/cm ²) (psi) | 153 | 223 | 186 | 269 |
| Std Dev. (10^3) | | | | |
| N/cm ² (psi) | 42 | 51 | 62 | 75 |
| Coeff of Var. (%) | | 23 | | 26 |
| Avg. w/o Boron | | 59 | | 69 |
| Avg. Modulus (10^6) | | | | |
| (N/cm ²) (psi) | 20.7 | 30 | No Data | |
| Std. Dev. (10^6) | | | | |
| (N/cm ²) (psi) | 2 | 3 | No Data | |

Table X

Individual Tensile Tests
 Substrate cleaned under Cl₂ at 1720°C
 Gage length = 2.54 cm (1 in.)

| Run Nos. | N227 | N230 | N237 | N242 |
|--|--|--|--|--|
| Parameters | $\gamma_2 \beta_1 T_3$ | $\gamma_2 \beta_1 T_4$ | $\gamma_2 \beta_1 T_4$ | $\gamma_2 \beta_1 T_3$ |
| Diameter (μ) (mils) | 63.5 2.5 | 68.6 2.7 | 63.5 2.5 | 63.5-81.3 2.5-3.2 |
| UTS (10^3) (N/cm ²)(psi) | 140 204 168 244 180 261 180 261 185 269 194 281 196 285 206 299 210 305 210 305 225 326 239 346 | 102 149 199 288 205 297 211 306 229 332 241 350 247 358 247 358 | 134 194 145 210 155 224 176 255 176 255 180 261 190 276 211 276 218 316 225 327 | 93 134 98 143 133 194 140 204 162 235 197 285 204 295 204 295 221 320 260 377 |
| Avg. UTS (10^3) (N/cm ²)(psi) | 194 282 | 210 305 | 181 262 | 171 248 |
| STD Dev. UTS (10^3) (N/cm ²)(psi) | 32 38 | 57 69 | 37 45 | 66 79 |
| Coeff. of Var. (%) | 14 | 23 | 17 | 32 |

TABLE XI

Strength, modulus and w/o boron for fiber produced from gas ratios γ_1 , γ_2 , and 1.77
 Substrate - As received GLRC Lot 1115 Spool #2 Gage Length for UTS data is 2.54 cm (1 in.)

| Run Nos. | N263 | N265 | N266 | N264 | N261 | N262 |
|---|--|--|--|--|--|---|
| Parameters | $\gamma_1 \beta_1^T$ | $\gamma_1 \frac{25 \text{ ft/hr}}{1080^\circ\text{C}}$ | $\gamma_1 \frac{25 \text{ ft/hr}}{1105^\circ\text{C}}$ | $1.77 \beta_1^T$ | $\gamma_2 \beta_1^T$ | $\gamma_2 \beta_1^T$ |
| Diameters (μ) (mils) | 58.4 | 2.3 | 59.7 | 2.35 | 63.5 | 2.5 |
| UTS (10^3) (N/cm ²) (psi) | 108 125 133 149 183 216 224 232 232 257 | 157 181 193 217 265 313 325 337 337 373 | 135 135 167 183 191 198 246 254 270 349 | 196 196 242 265 276 288 357 369 392 507 | 61 92 143 234 244 263 337 346 357 371 | 96 110 124 138 179 207 220 234 262 262 |
| Avg. UTS (10^3) (N/cm ²) (psi) | 186 | 270 | 213 | 309 | 169 | 245 |
| Std. Dev. (10^3) (N/cm ²) (psi) | 65 | 78 | 81 | 97 | 94 | 113 |
| Coeff. of Var. (%) | 29 | 32 | 46 | 34 | 31 | 14 |
| Avg. Modulus (10^6) (N/cm ²) (psi) | 33 | 49 | 32 | 46 | 33 | 48 |
| Std. Dev. (10^6) (N/cm ²) (psi) | 3 | 4 | 1 | 2 | 1 | 1 |
| Avg. w/o Boron | 75 | 75 | 75 | 70 | 68 | 67 |
| CH ₄ /BCl ₃ | 0.44 | 0.44 | 0.44 | 1.77 | 2.34 | 2.34 |

Table XII

Density of Monofilament With Various W/O Boron

| <u>Run No.</u> | <u>W/O Boron in Deposit</u> | <u>Density (g/cc)</u> |
|----------------|-----------------------------|-----------------------|
| N232 | 59 | 2.079 |
| N262 | 65 | 2.188 |
| N266 | 75 | 2.226 |

CHEMICAL VAPOR DEPOSITION REACTOR

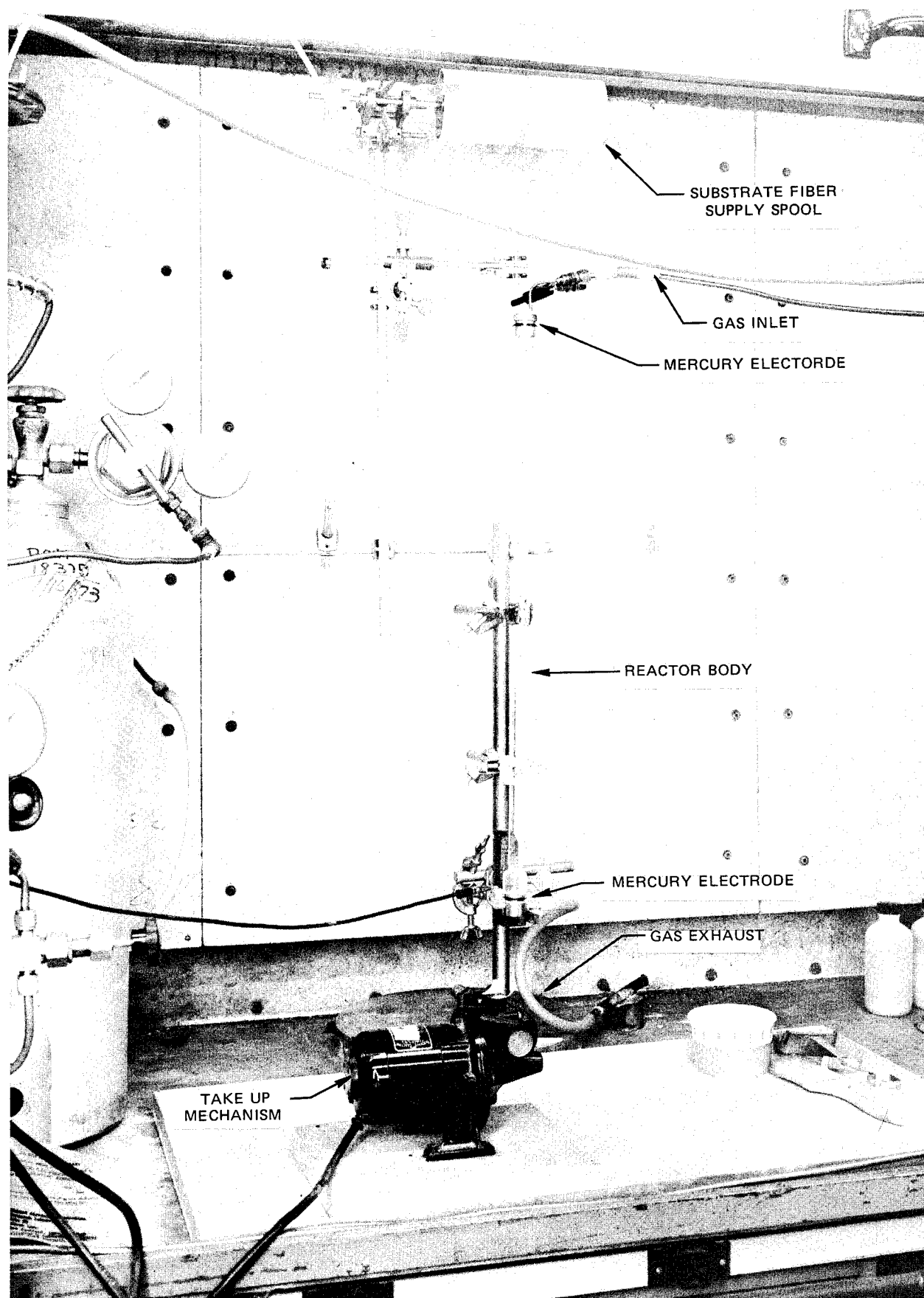
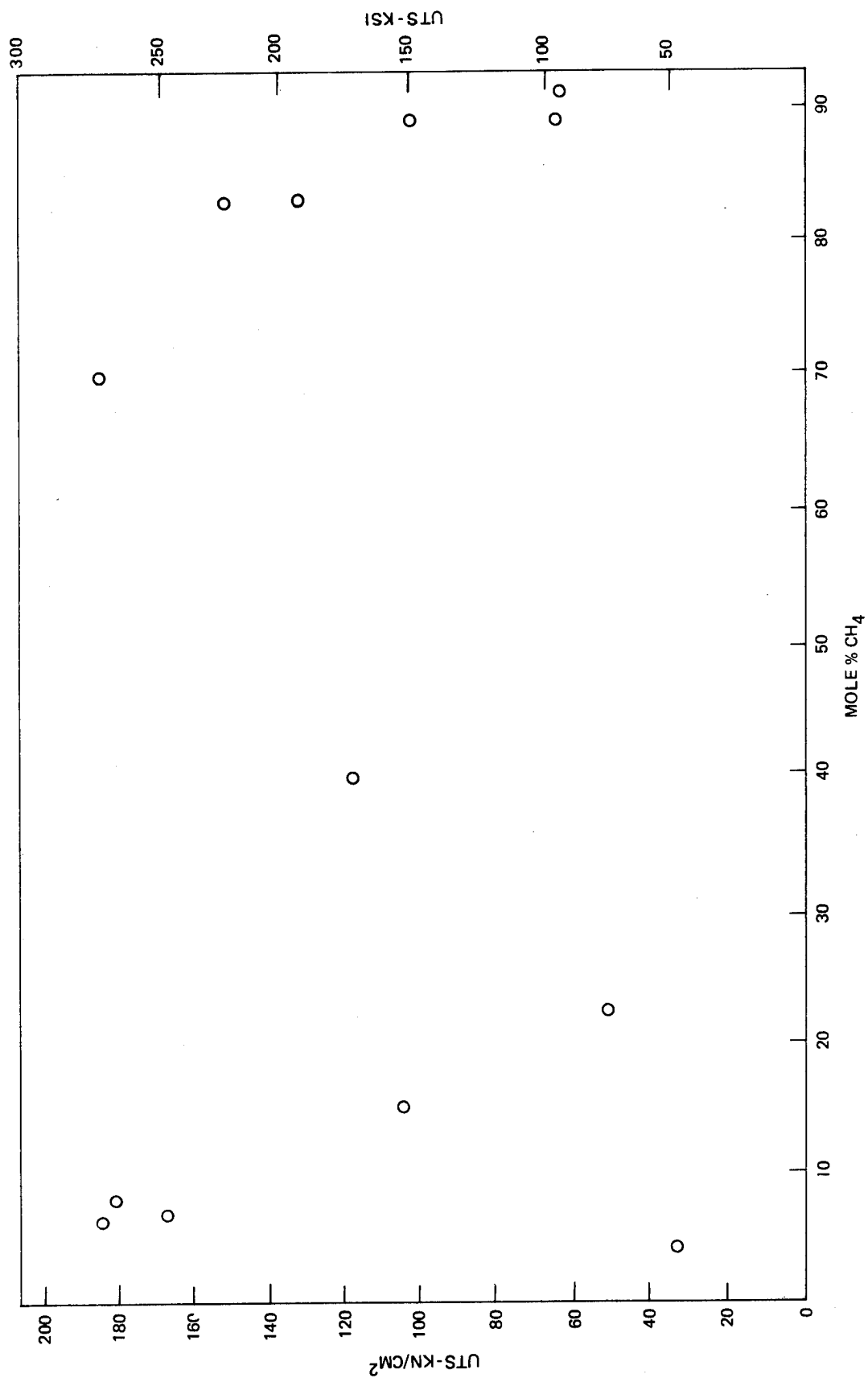


FIG. 2

UTS VS MOLE % CH₄ FOR C (B) FIBER

CH₄, BCl₃, H₂ SYSTEM



PHOTOGRAPHS OF SURFACES OF STRONG CARBON-BORON ALLOY MONOFILAMENT

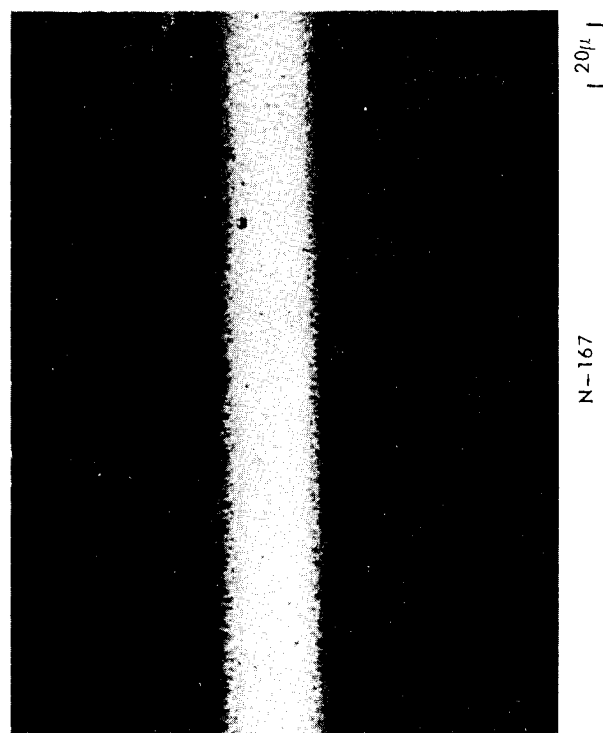
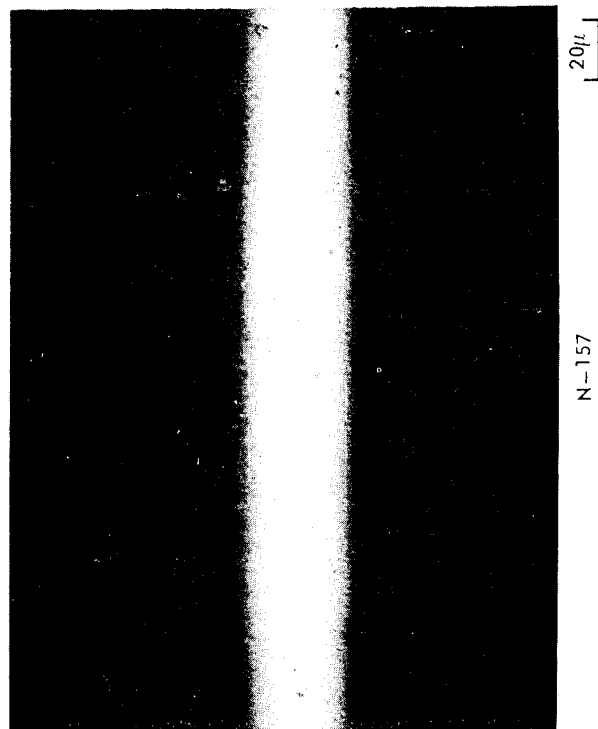
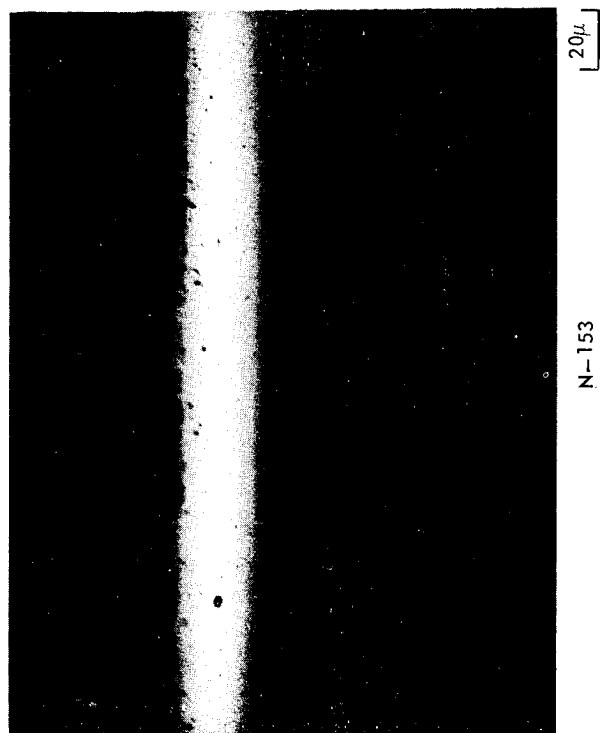
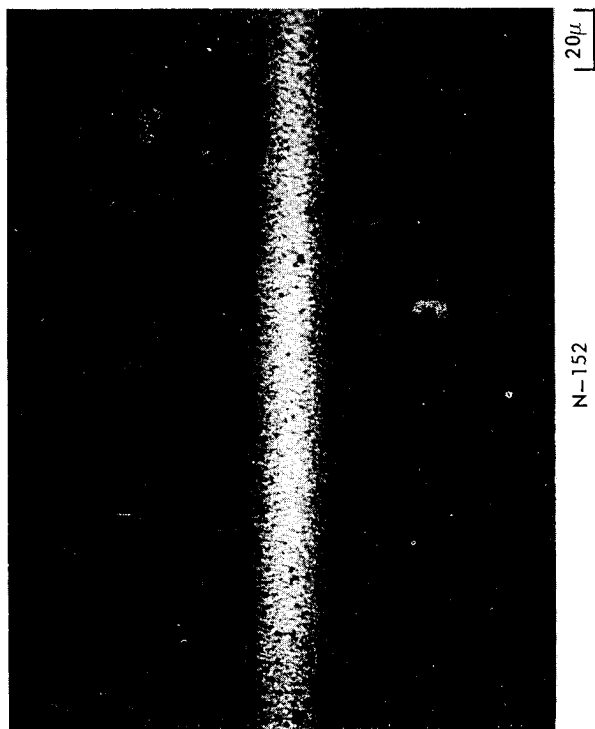
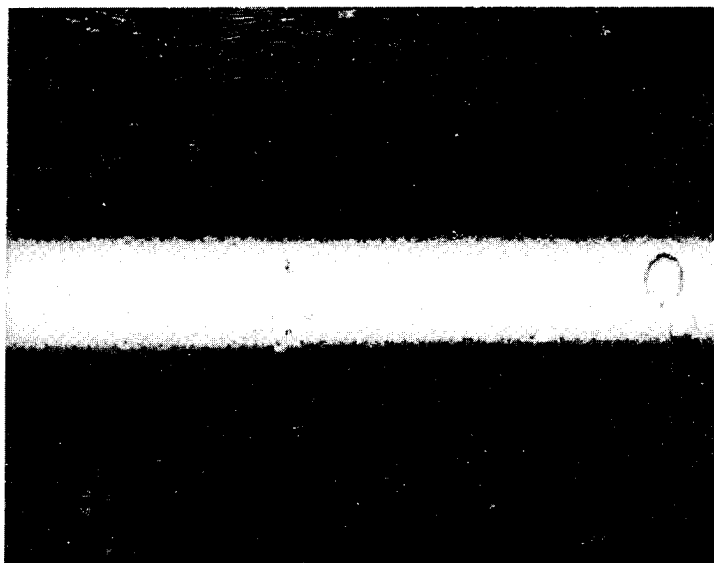


FIG. 3

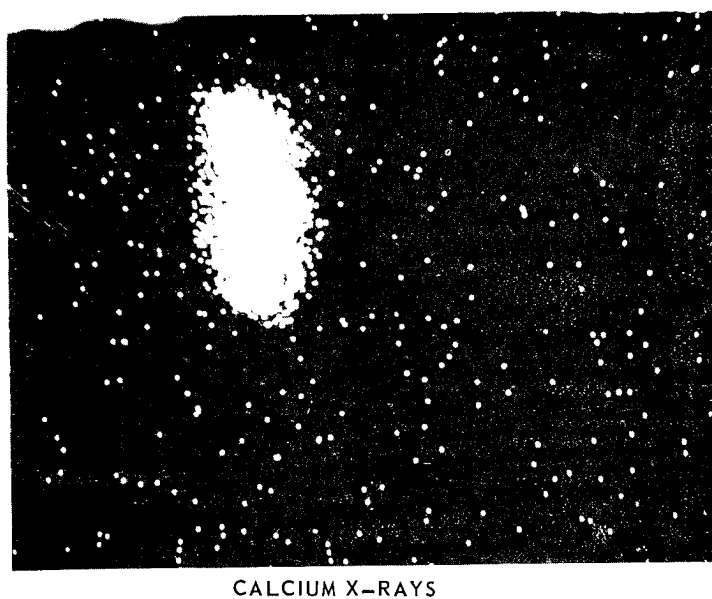
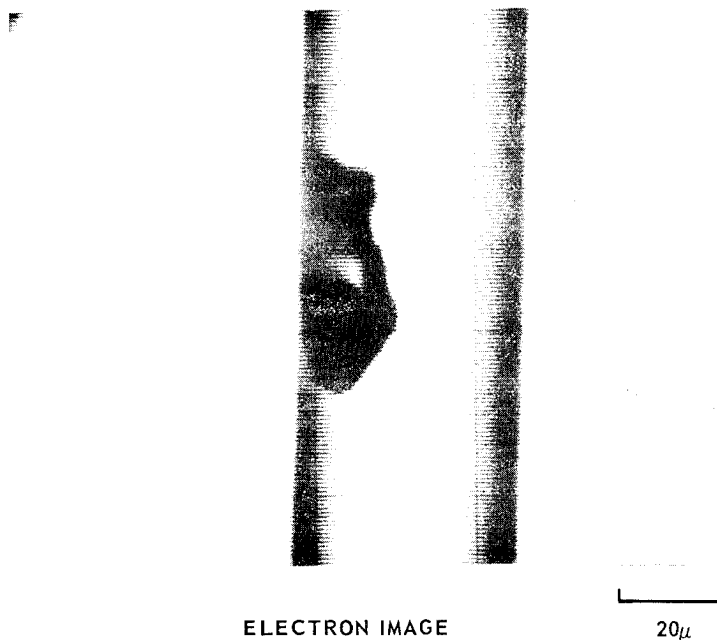
PHOTOGRAPHS OF SURFACE OF WEAK CARBON-BORON ALLOY
MONOFILAMENT



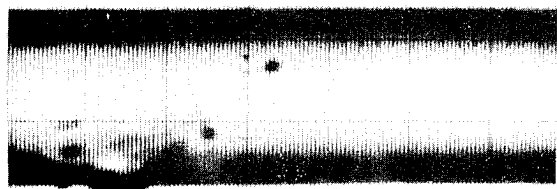
N 190

20μ

ELECTRON IMAGE AND DISTRIBUTION PHOTOGRAPHS OF A PORTION
OF THE BORON-CARBON ALLOY MONOFILAMENT SURFACE

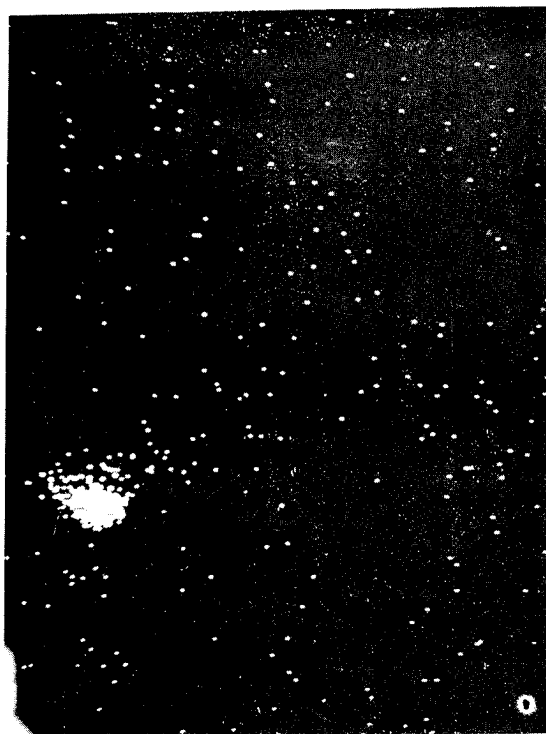


ELECTRON IMAGE AND X-RAY DISTRIBUTION PHOTOGRAPH OF A PORTION OF THE "AS RECEIVED"
CARBON SUBSTRATE FIBER SURFACE

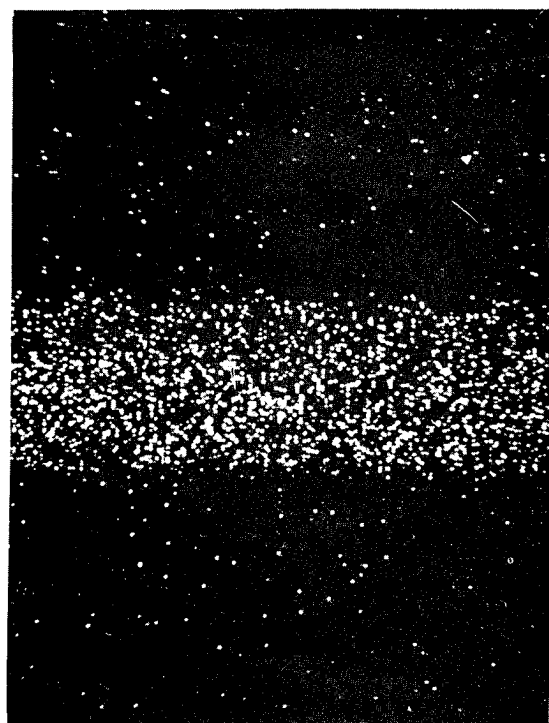


ELECTRON IMAGE

20 μ



SILICON X-RAYS



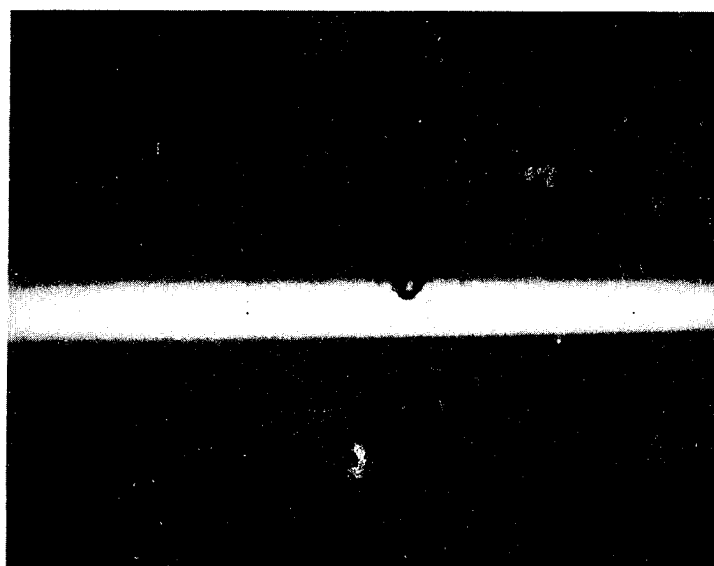
SULFUR X-RAYS



POTASSIUM X-RAYS

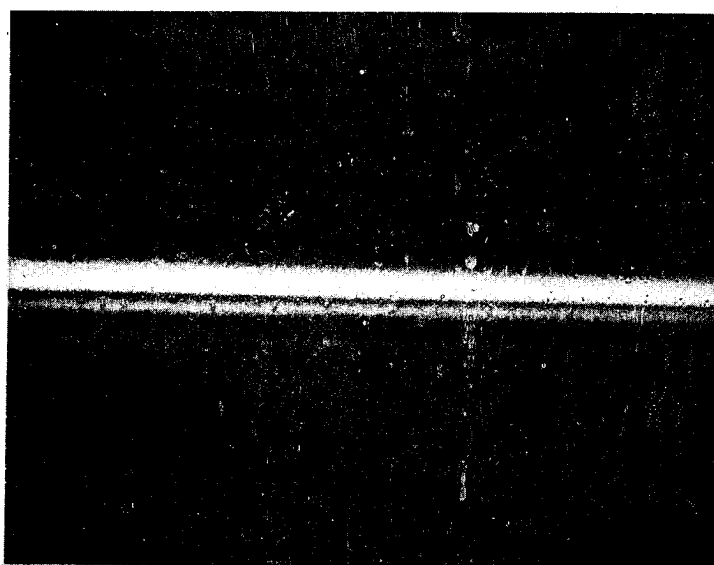
FIG. 6

PHOTOMICROGRAPH OF A SECTION OF THE "AS RECEIVED" CARBON SUBSTRATE
FIBER AND A SECTION OF THE "AS RECEIVED" CARBON SUBSTRATE FIBER CLEANED
UNDER Cl_2 AT 1650°C



AS RECEIVED

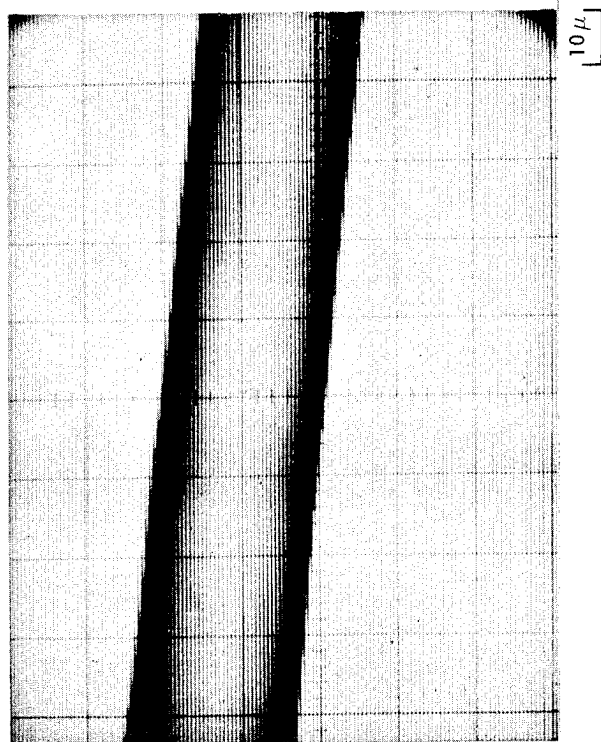
20 μ



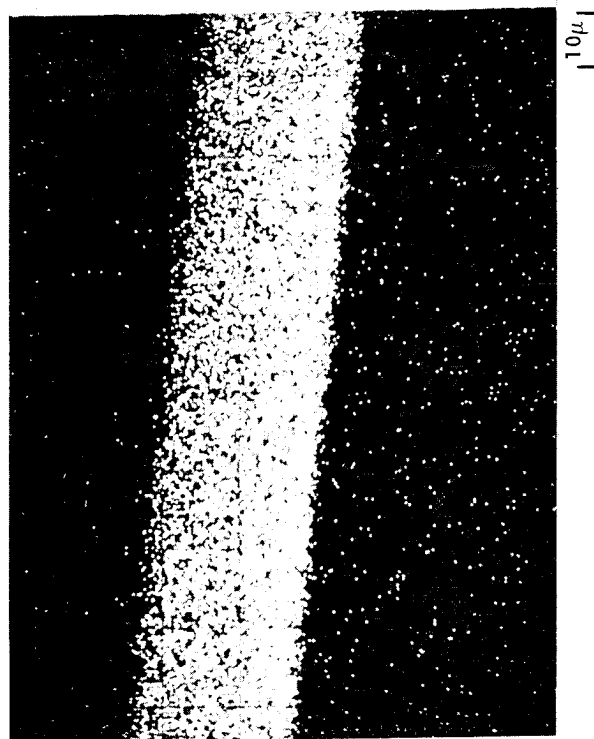
CLEANED UNDER Cl_2 AT 1650°C

20 μ

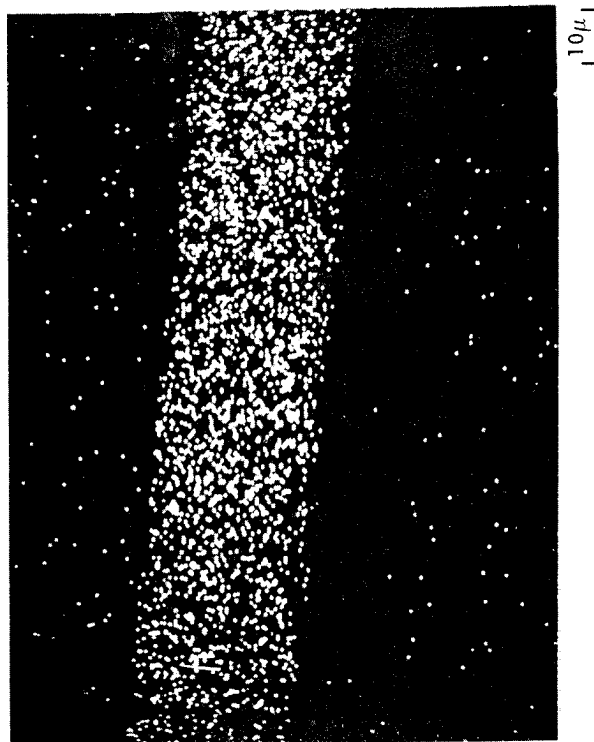
ELECTRON IMAGE AND X-RAY DISTRIBUTION PHOTOGRAPHS OF A PORTION OF THE FILAMENT CLEANED IN Cl_2 AT 1650°C



ELECTRON IMAGE



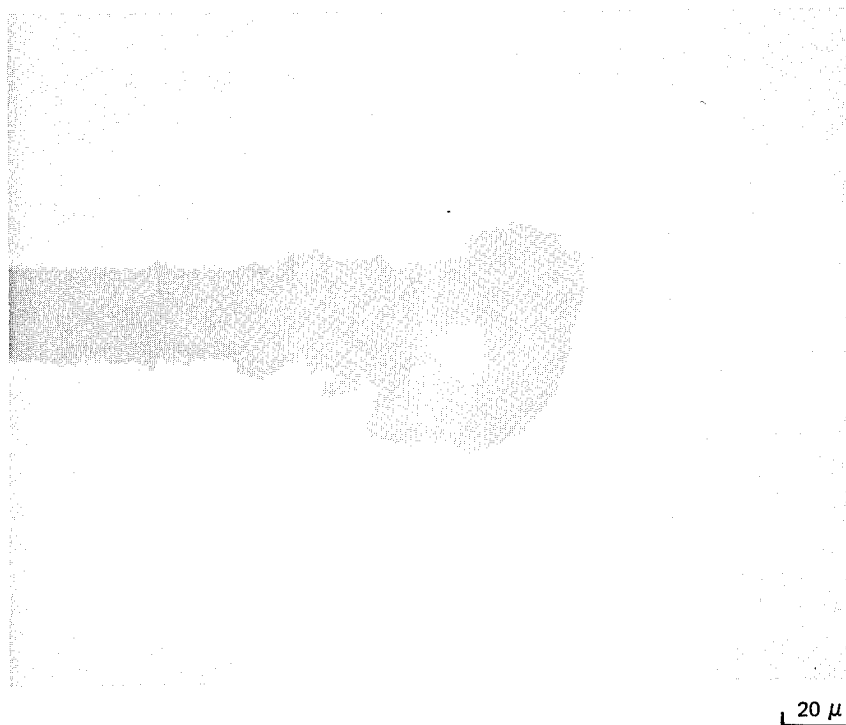
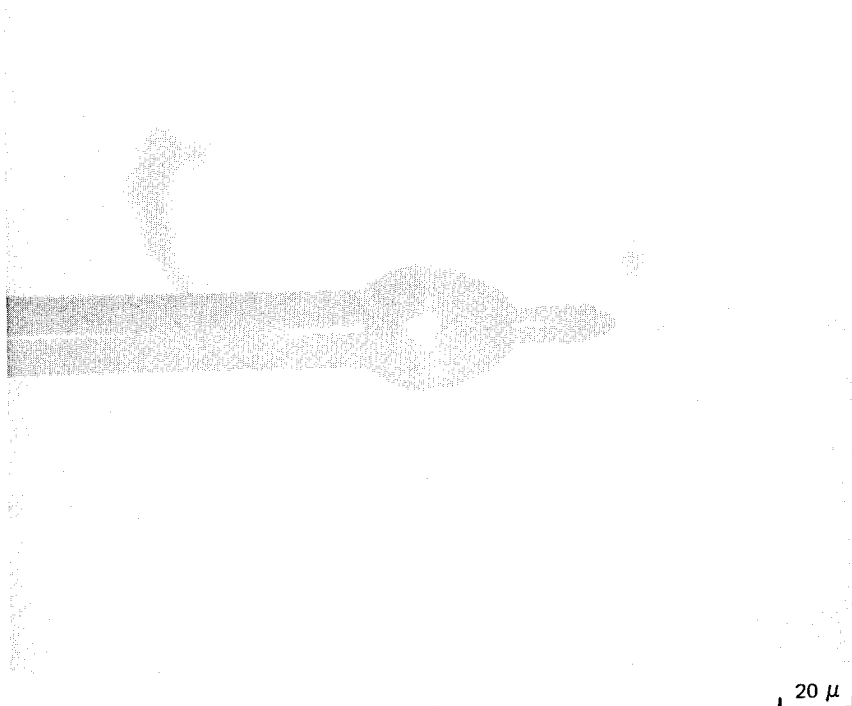
CARBON X-RAYS



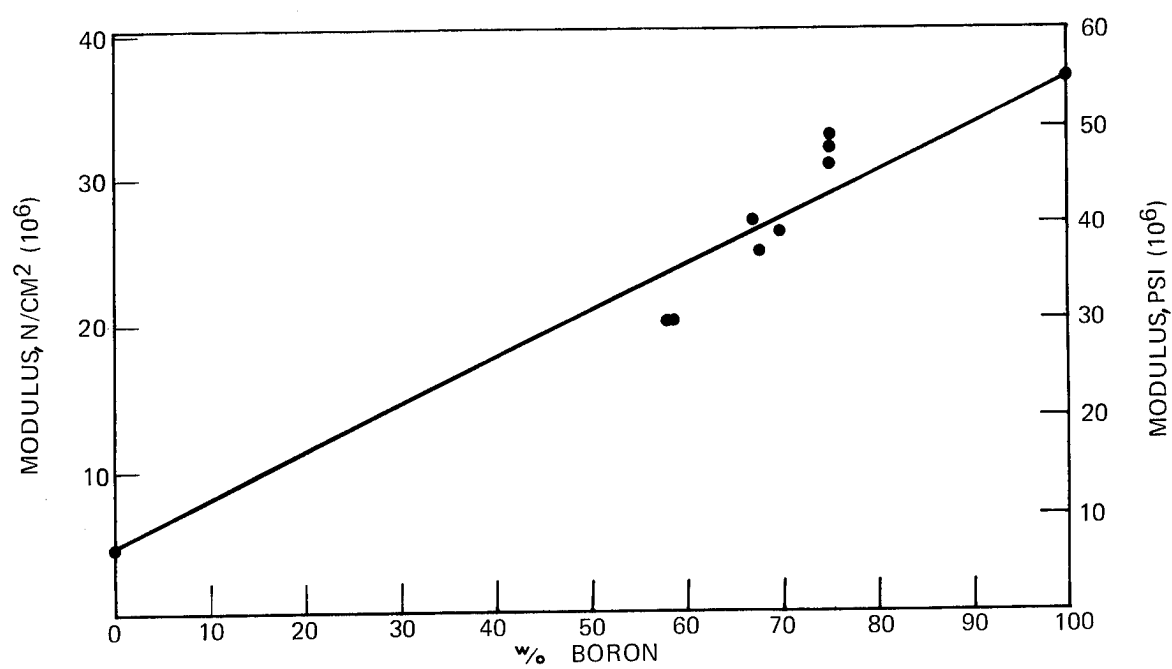
SULFUR X-RAYS

FIG. 8

PHOTOGRAPHS OF MONOFILAMENT BREAKS
THAT OCCUR WITHIN THE REACTOR

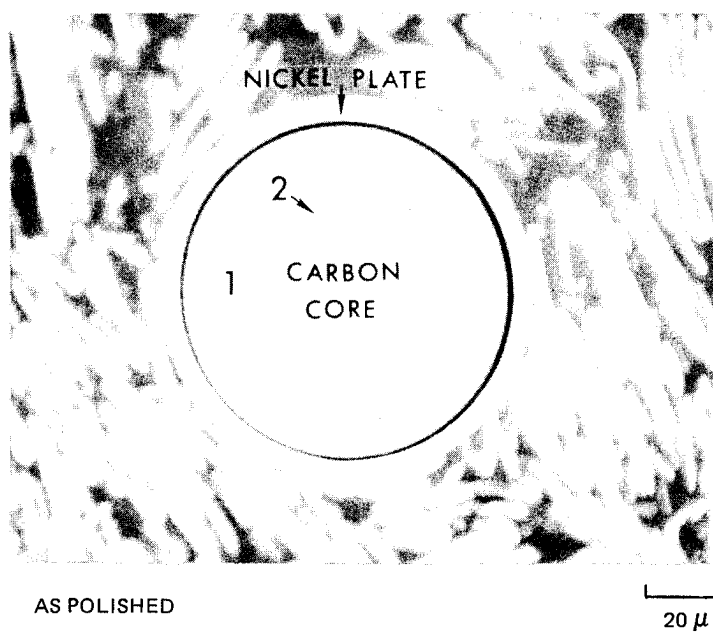


MODULUS VS % BORON CARBON-BORON ALLOY MONOFILAMENT



RESULTS OF POINT COUNT ANALYSES OF THREE FIBERS,
A REPRESENTATIVE FIBER BEING SHOWN IN THIS FIGURE

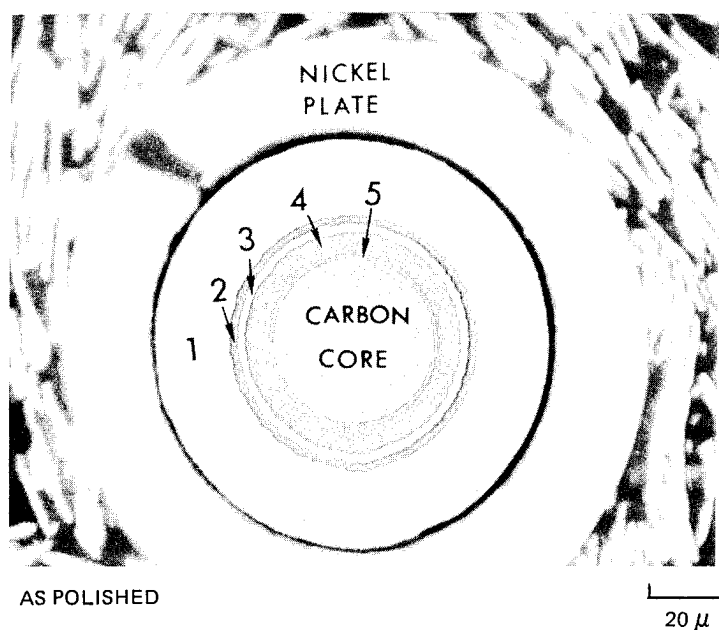
CH_4/BCl_3 RATIO = 5
POWER APPLIED = 246 WATTS



| | | CONCENTRATION w/o (a/o) | |
|-------|------------|-------------------------|-------------|
| ZONE | | BORON | CARBON |
| NO. 1 | OUTER ZONE | 36.8 (39.3) | 63.2 (60.7) |
| NO. 2 | INNER ZONE | 32.5 (34.8) | 67.5 (65.2) |

RESULTS OF POINT COUNT ANALYSES OF THREE FIBERS,
A REPRESENTATIVE FIBER BEING SHOWN IN THIS FIGURE

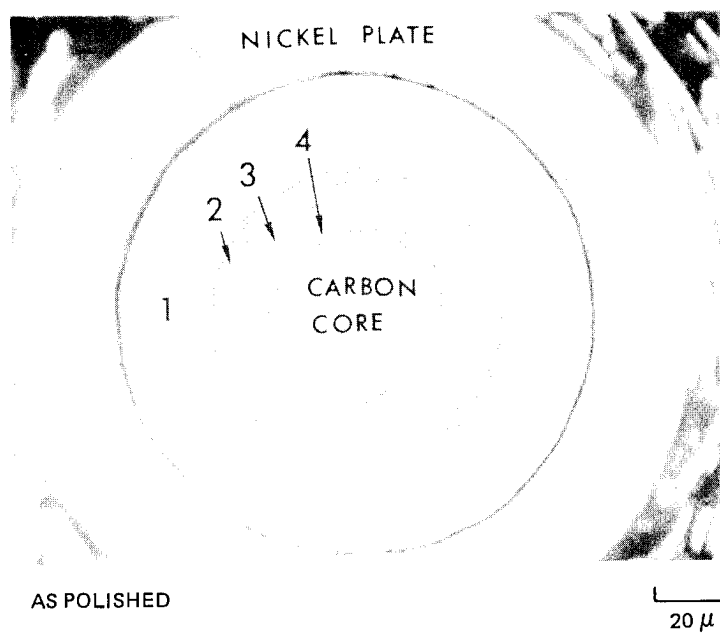
CH_4/BCl_3 RATIO = 5
POWER APPLIED 264 WATTS



| | | CONCENTRATION | |
|-------|----------------------|---------------|-------------|
| | | w/o (a/o) | |
| ZONE | | BORON | CARBON |
| NO. 1 | THICK OUTER ZONE | 40.0 (42.6) | 60.0 (57.4) |
| NO. 2 | DARK THIN ZONE | 21.9 (23.7) | 78.2 (76.3) |
| NO. 3 | LIGHT THIN ZONE | 50.2 (52.8) | 49.8 (47.2) |
| NO. 4 | DARK INNER ZONE | 29.4 (31.6) | 70.7 (68.4) |
| NO. 5 | VERY THIN INNER ZONE | 17.4 (19.0) | 82.6 (81.0) |

RESULTS OF POINT COUNT ANALYSES OF THREE FIBERS, A REPRESENTATIVE FIBER
BEING SHOWN IN THIS FIGURE

CH_4/BCl_3 RATIO = 5
POWER APPLIED 300 WATTS



CONCENTRATION w/o (a/o)

| <u>ZONE</u> | | <u>BORON</u> | <u>CARBON</u> |
|-------------|------------------|--------------|---------------|
| NO. 1 | OUTER ZONE | 43.7 (46.3) | 56.3 (53.7) |
| NO. 2 | WHITE INNER ZONE | 60.0 (58.2) | 44.1 (41.5) |
| NO. 3 | DARK INNER ZONE | 37.6 (40.1) | 62.4 (59.9) |
| NO. 4 | VERY INNER ZONE | 23.8 (25.8) | 76.2 (74.3) |